The author states that the results already obtained by this instrument have been so satisfactory as to leave him no cause to regret the time that has been devoted to, or the expense that has been incurred in the construction of this truly beautiful apparatus.

A full description of the instrument is introduced, with several diagrams showing the construction and adaptation of the different parts of the apparatus, and two drawings, one showing the general appearance of the instrument when prepared for observation, and the other representing it as seen when viewed from above.

## II. THE BAKERIAN LECTURE.—"On the Direct Correlation of Mechanical and Chemical Forces." By Henry Clifton Sorby, F.R.S. Received April 29, 1863.

Perhaps it may be thought somewhat strange that a geologist should undertake such a subject as the correlation of forces; but the very fact of my being a geologist has led to the investigations of which I now purpose to give a short preliminary account. In studying general chemical and physical geology, and especially in examining the microscopical structure of rocks, I have for a number of years been greatly perplexed with a class of facts which pointed both to a mechanical and to a chemical origin. At first I attributed them either to a mechanical or a chemical action, or to the two combined; but in most cases no satisfactory explanation could be given. At length, however, facts turned up which altogether precluded any supposition not involving direct correlation; for they most clearly indicated that mechanical force had been resolved into chemical action in the same way as, under other circumstances, it may be resolved into heat, electricity, or any other modification of force, as so ably described by Grove in his work 'On the Correlation of Physical Forces.'

The effect of pressure on the solubility of salts has already been made the subject of speculation and experiment \*, and a considerable number of facts have been described, showing that pressure will more

<sup>\*</sup> Perkins, Ann. de Chim. et de Phys. vol. xxiii. p. 410. Sartorius von Waltershausen, Göttinger Studien, 1857. Bunsen, Ann. der Chem. und Pharm. 1848, vol. lxv. p. 70. Favre, Comptes Rendus, vol. li. p. 1027. Thomson, Proc. Roy. Soc. vol. xi. p. 473 (1861).

or less influence such chemical actions as are accompanied by an evolution of gas, so that it may cause a compound to be permanent which otherwise would be decomposed\*; but the results were for the most part so indefinite and unconnected, or of such a character, that Mr. Grove does not allude to the direct production of chemical action from mechanical force. That this is, however, extremely probable will be evident to all who have considered the manner in which the various physical forces are correlated; for if mechanical force can be produced by chemical action, why should not the converse be true? In this paper I shall endeavour to show that such is really the fact, and that in some cases the mechanical equivalent of the chemical force may be determined.

In order to obtain the necessary great pressure, I have made use of a modification of the method employed by Bunsen; but instead of filling the tubes at the ordinary temperature of the atmosphere and then gently heating them for several hours, I in the first instance filled them at a temperature 10° or 20° C. lower, so that when finally sealed up they contained considerably more liquid than they could hold without pressure at the ordinary temperature of the atmosphere at the time being; and thus, by its tendency to expand, this liquid and anything enclosed in the tube were subjected to a very great pressure. By keeping the tubes in various parts of the house, according as the weather varied, I have been able to maintain for several weeks or even months a pressure of, for instance, about 100 atmospheres, as measured by means of a capillary-tube pressure-gauge enclosed within the larger tube. Since in all cases I had a second tube which from first to last was treated precisely like the other, pressure excepted, I have been able to determine the effect produced by the pressure with very considerable accuracy—at all events so as to leave no doubt whatever about the general facts. At the same time I wish it to be understood that the results described below must be looked upon only as approximations to the truth.

<sup>\*</sup> Sir James Hall, Trans. Roy. Soc. Edinb. 1812, vol. vi. p. 71. Wöhler, Ann. der Chem. und Pharm. vol. xxxiii. p. 125. Babinet, Ann. de Chim. et de Phys. (2) vol. xxxvii. p. 183. Lothar Meyer, Pogg. Ann. vol. civ. p. 189. Beketoff, Comptes Rendus, vol. xlviii. p. 442. Gassiot, Brit. Assoc. Report, 1854, p. 39. Favre, Comptes Rendus, vol. li. p. 1027. Berthelot et Péan de Saint-Gilles, L'Institut, 1862, p. 257. Gmelin's Handbook of Chemistry, published by the Cavendish Society, vol. ii. p. 293.

I will first call attention to the well-known influence of pressure on the fusing-point of various substances, since it is a connecting link between well-established facts and those I am about to describe. Bunsen\* and Hopkins† have shown that substances which expand when fused have their point of fusion raised by mechanical pressure; that is to say, since mechanical force must be overcome in melting, the tendency to melt must be increased by heat before that opposition can be overcome; and the pressure required to keep them solid at any temperature above their natural point of fusion may be looked upon as the mechanical representative of the force with which they tend to fuse at that temperature. Professor W. Thomson T has shown that, on the contrary, water, which expands in freezing, has its point of fusion lowered by pressure; that is to say, since mechanical force must be overcome in crystallizing, crystallization will not take place under increased pressure unless the force of crystalline polarity be increased by reducing the temperature. Thus, calculating from his experiments and from the known latent heat of ice, and assuming that no heat is gained or lost by contact with external objects, if we had 1 part of ice and 100 of water at 0° C., and then applied a pressure of 103 atmospheres, the ice would, as it were, dissolve in the water, the whole would become liquid, and the temperature be reduced to - 792° C.; or, in other terms, at that temperature the tendency to crystallize is exactly counterbalanced by that pressure.

Now I find that similar principles hold true with respect to the solubility of salts in water. If, when they dissolve, the total bulk increases, pressure reduces their solubility; whereas if the bulk decreases, pressure makes them more soluble; in other words, solution or crystallization is impeded by pressure according as mechanical force must be overcome in dissolving or in crystallizing.

Various authors have written on the volume with which salts enter into solution §; but since the subject before us requires a different

- \* Pogg. Ann. 1850, vol. lxxxi. p. 562.
- † British Association Report, 1854, p. 57.
- ‡ Trans. Roy. Soc. Edinb. vol. xvi. p. 575.

<sup>§</sup> Playfair, Chem. Soc. Quart. Journ. vol. i. p. 139. Michel and Krafft, Ann. de Chim. 2 sér. vol. xli. p. 471. Schiff, Ann. der Chemie, vol. cix. p. 325; vol. cxi. p. 68; vol. cxiii. p. 349. Gerlach, Specifische Gewichte der Salzlosungen, &c., 1859. Tissier, L'Institut, 1859, p. 158; 1860, p. 281. Kremers, Pogg. Ann. vol. lxxxv. pp. 37 and 246; vol. xciv. p. 87; vol. xcv. p. 110; vol. xcvi. p. 39; vol. cv. p. 360; vol. cviii. p. 115. Billet, Thèse de Chimie.

class of facts to be taken into account, I shall base my conclusions on my own experiments. The volume with which salts exist when in solution, assuming that of the water to remain unchanged, varies greatly in the case of different salts, and also according to the amount in solution and the temperature. Thus, taking sal-ammoniac as an example, when there are 3 per cent. in solution the volume is as if it expanded 3.40 per cent. on dissolving; whereas when 25.55 per cent. are in solution, the expansion is 11.36 per cent.; and when nearly concentrated at about 13° C., an additional quantity expands on dissolving 15.78 per cent. In by far the greater number of cases, however, there is a contraction on dissolving, and the amount gradually diminishes for each additional quantity entering into solution, so that the mean result is very different from what occurs when the solution is dilute or nearly saturated. It is this contraction or expansion when a small additional quantity is dissolved in a nearly concentrated solution that must be taken into account in the following calculations.

In determining the influence of pressure on the solution of salts, I found it requisite to adopt somewhat different methods according to the peculiarities of the salts. In some cases I sealed up in a saturated solution portions of the salt in clean, solid crystals, and determined the effect due to pressure from their loss in weight; whereas in other cases I sealed up solutions containing more salt than could be dissolved at the temperature at which the experiments were made, and determined the effect of pressure from the difference in the weight of the crystals deposited; being of course careful to make allowance for any difference in the amount of solution in the tube with pressure and in that without, and to avoid any error that might be produced by a different temperature. In all cases I have had a tube with pressure and another without, treated from first to last in precisely the same manner, and kept at exactly the same temperature, so that pressure was the only difference; and usually the effect was so well marked that there was no doubt about the result. In the case of chloride of sodium, solution goes on so slowly, and the mechanical equivalent of the force of crystallization is so great, that if pressure had been applied for only a few hours one might have concluded, with Bunsen, that pressure has no influence on solubility; but, by maintaining it for a week or more, there was no difficulty whatever

in perceiving that a solution which was quite saturated without pressure, dissolved more under a pressure of about 100 atmospheres.

The solubility of a salt in water appears to me to result from a kind of affinity which decreases in force as the amount of salt in solution This affinity is opposed by the crystalline polarity of the salt; and when the two forces are equal, the solution is exactly saturated. As is well known, a change in temperature alters this equilibrium; and, according to my experiments, mechanical pressure relatively increases one or other of these opposing forces, according to the mechanical relations of the salt in dissolving. At all events in the case of chloride of sodium the extra quantity dissolved under pressure varies directly with it for such pressures as glass tubes will resist, in the same manner as, according to Thomson's experiments, the fusing-point of ice is reduced. Thus I found that for a pressure of 49½ atmospheres the extra solubility was 176 per cent., and for 121 atmospheres '431, which are almost exactly in the same ratio. Hence, if S be the amount soluble without pressure, under a pressure of p atmospheres the solubility at the same temperature would be S+ps, where the values of S and s are independent, and vary for different temperatures and different salts. Future experiments may perhaps show that this conclusion should be modified; but yet it will be well to adopt it provisionally, in order to compare together the mechanical relations of different salts which otherwise would not be so intelligible.

According to Michel and Krafft\* and to Schiff†, sal-ammoniac is the only salt known for certain to occupy more space in solution than when crystallized. Hence under pressure mechanical force must be overcome in dissolving, and experiment shows that, on this account, the relative force of crystalline polarity is increased and the solubility decreased. This is the reverse of what results from an elevation of the temperature, so that the effect cannot be due to heat generated by the pressure, but must be the direct consequent of pressure. Calculating from an experiment where the pressure was 164 atmospheres, which gave a decreased solubility of 1.045 per cent. of the whole salt in solution, a pressure of 100 atmospheres would cause 637 per cent. less to be dissolved than is soluble at 20° C. without pressure, and the pressure requisite to reduce the solubility to the extent of 1 per cent.

<sup>\*</sup> Ann. de Chim. 3 sér. vol. xli. p. 471.

<sup>†</sup> Ann. der Chemie, vol. cix. p. 325; vol. cxiii. p. 329.

would be 157 atmospheres. Expressing this fact in other words, we may say that a pressure of 157 atmospheres is the mechanical force with which the salt tends to dissolve in a solution containing 1 per cent. less than can dissolve at the same temperature without pressure, because the two forces exactly counterbalance one another. In a still more dilute solution the force would of course be still greater, in accordance with the fact of a greater pressure being necessary to prevent the salt from being dissolved. Supposing then that we had a solution a trifle more dilute than that just named, and in such indefinitely large quantity that a cubic inch of the salt could dissolve in it and yet produce no sensible change in its strength, so that from first to last it might be considered to dissolve under a pressure of 157 atmospheres, and also supposing that it was rigidly enclosed on all sides but one, so that the whole expansion must take place in one direction over an area of one square inch, since on dissolving there is an increase in bulk from 100 to 115.78, the solution of this cubic inch would, as it were, raise 2355 lbs. through the space of .1578 inch. This is mechanically the same as  $371\frac{1}{2}$  lbs. raised 1 foot, or, the specific gravity of the salt being 1.53, the same as 171 times the weight of the salt itself raised Since it involves no arbitrary unit but the metre, I shall adopt the last expression as the measure of the total amount of mechanical work done by the solution of salts which expand in dissolving, and which may conversely be looked upon as the measure of the mechanical force rendered latent and, as it were, expended in the act of crystallization when crystals are deposited. of this mechanical equivalent of course varies with the strength of the solution, as already remarked.

In the case of salts which occupy less space when dissolved than when solid, pressure, like the increased temperature, causes them to be more soluble; mechanical force is lost when they dissolve, and is, as it were, expended in giving rise to solution. When water thus containing more of a salt than could otherwise be dissolved at the same temperature is just saturated under any given pressure, the amount of pressure represents the force of crystalline polarity tending to cause the salt to be deposited in a crystalline form, but which is exactly counterbalanced by that pressure. I will not give the details for each salt, but subjoin a Table of the results at which I have arrived for such as illustrate particular points of interest, the calculations being all made

in accordance with the principles already described. I also give them in the case of water, calculated from Thomson's experiments, assuming that, when ice melts and mixes with water, it may be looked upon as dissolving in it; and, as will be seen, the mechanical force thus deduced is of the same general order of magnitude as that generated by the crystallization of salts.

	I.	II.	III.	IV.	v.
1. Chloride of Sodium	13.57	97	•407	.419	157
2. Sulphate of Copper	4.83	60	1.910	3.183	7
3. Ferridcyanide of Potas-					
sium	2.51	86	.288	<b>·</b> 335	42
4. Sulphate of Potash	31.21	63	1.840	2.914	42
5. Ferrocyanide of Potas-					
sium	8.90	66	1.640	2.485	20
6. Water	8.93			•991	106

Nos. 2 and 5 are calculated as hydrated crystals.

Column I. gives the expansion of each salt in crystallizing from a nearly saturated solution in water, the volume in a crystalline state being taken at 100.

Column II. gives the actual pressure in atmospheres in the experiment.

Column III. gives the increased solubility due to the pressure given in column II., the total amount of salt dissolved without pressure being taken at 100.

Column IV. gives the increase in solubility that would be produced by a pressure of 100 atmospheres, as calculated in accordance with the principles already described, the same unit being taken as in column III.

Column V. gives the value of the mechanical work that could be done, or, so to speak, the amount of mechanical force set free when the various substances crystallized from a solution containing 1 per cent. more than would be dissolved without pressure, as measured by the number of times its own weight which any unit of the various salts could raise to the height of 1 metre in the act of crystallization. Conversely, it is the amount of mechanical force which becomes latent in the act of solution; and in the case of a still more supersaturated solution it would be greater, and vice versa, in accordance with the fact of the increased solubility varying with the pressure.

On comparing together the various salts, it will be seen that their properties vary very considerably. Thus, under the same pressure, the extra quantity of sulphate of copper dissolved in nearly ten times that of ferridcyanide of potassium. The mechanical equivalents also vary even more, being (for chloride of sodium) about  $22\frac{1}{2}$  times as great as for sulphate of copper. On the contrary, the mechanical equivalents of ferridcyanide of potassium and sulphate of potash are the same; but, under equal pressures, the extra quantity of the latter dissolved in nearly nine times as great, owing to the difference in the amount of expansion in crystallizing. This latter is, however, nearly the same for water and ferrocyanide of potassium, whilst, under the same pressure, the extra quantity of that salt dissolved is 2½ times that of ice, in consequence of the much greater mechanical equivalent of the ice. It appears to me that we may provisionally conclude that the increased solubility due to pressure varies directly with the change of volume, and inversely with the mechanical equivalent of the force of crystalline polarity, so that, if S be the total amount of salt which dissolves without pressure, c be some function of the change in volume in dissolving, and m some function of the mechanical equivalent of the force of crystalline polarity, the solubility, at the same temperature, under a pressure of p atmospheres would be  $S + \frac{p \cdot c}{m}$ . If the salt be one that expands on dissolving, c of course is negative, and therefore under pressure the solubility becomes  $S = \frac{p \cdot c}{m}$ ; that is to say, it is diminished, as proved by experiments with sal-ammoniac. If no change in volume took place, we may, I think, also conclude that pressure would not in any way increase or decrease the solubility of a salt. Moreover, since, when a solution is just saturated, the force with which the salt tends to crystallize is equal to that with which it tends to dissolve, their mechanical equivalents must be equal and opposite. Hence we may perhaps conclude that, other circumstances being the same, the mechanical equivalent of a salt like chloride of sodium, which so readily attracts moisture, would be greater than that of one like sulphate of copper, which so readily loses even its water of crystallization; and thus also the relative influence of equal amounts of

pressure would be very different, as is confirmed by experiment in the case of these and some other salts.

The facts I have described, therefore, show that there is a direct correlation between mechanical force and the forces of crystallization and solution. According to some chemists, the latter is an instance of real combination; but, whatever views be entertained respecting its nature, we cannot, I think, deny that the force represents some modification of chemical affinity, or is at all events most closely allied to it. In comparison with some kinds of affinity, it may indeed be, and probably is, weak; but yet, as I have shown, it sometimes has a very considerable mechanical equivalent, even when nearly counterbalanced by an opposite force; and since such pressures as glass tubes will resist have no very great influence on what we may perhaps consider a weak affinity, we cannot expect that any pressure at our command would have much influence on strong affinities. I have, however, succeeded in obtaining some results which apparently show that pressure influences undoubtedly chemical changes taking place slowly, and therefore probably due to weak, or nearly counterbalanced, affinities.

The method adopted in this part of the inquiry was to seal up some solid substance in a solution which gives rise to a slow double decomposition, taking great care to have in the tube with pressure, and in that without, pieces cut so as to be of the same size and form, and a solution of the same character, so that, with the exception of pressure, all the conditions were the same. Possibly I may be so fortunate as to discover some case where the affinity is so weak that pressure may determine whether it go forward or not, of which fact the structure of metamorphic rocks furnishes examples; but hitherto I have only been able to prove that pressure modifies the rate at which chemical action takes place. This branch of the inquiry is, however, beset with many difficulties, for the change in volume produced by double decomposition is small, and its determination involves several complicated questions. The volume of the solids is easily determined; but that of the salts in solution is not the same when other salts are present as when they are dissolved in pure water, and varies much according to the strength of the solution and the nature of the salts; and many points are still so obscure, that I shall only give two cases by way of example.

When a portion of Witherite is enclosed in a tube with a strong solution of protochloride of iron, there is a slow decomposition into chloride of barium, which is dissolved, and carbonate of iron, which remains firmly attached to the Witherite, and would ultimately give rise to an excellent pseudomorph. The best conclusion at which I have been able to arrive is, that there is in this change an increase in volume equal to about 10.7 per cent. of the Witherite altered, so that, under pressure, mechanical force must be overcome. experiment where everything went on in a very satisfactory manner, the pressure was maintained for three months at from 80 to 100 atmospheres, and for one month was under 80 atmospheres, so that, on an average, it was about 80 atmospheres; and I found that the amount of chemical change was 21.7 per cent. less than when, all other circumstances having been the same, there had been no pressure; thus clearly showing that pressure had, as it were, diminished the force of chemical affinity. If then one cubic inch had been altered under this pressure, it would have overcome a mechanical force equal to that required to raise 1200 lbs. through the space of .107 inch. which is equivalent to raising twenty-one times its own weight to the height of 1 metre; and under the same circumstances 1.278 cubic inch would have been altered when no such mechanical force had to be overcome. Supposing then that in both cases the total energy at work was the same, but in one was altogether expended in producing a chemical result, and in the other in producing partly a chemical and partly a mechanical effect, we may say that the force which gives rise to the purely chemical change, taking place at a particular rate, is equal to that which gives rise to this chemical effect, taking place at '783 of that rate, and to a mechanical effect equal to the force required to raise in the same space of time 34.87 times the weight of the Witherite altered to the height of 1 metre. Supposing also that the power of chemical force varies as the rate at which it gives rise to a chemical change, in the same manner as the power of a mechanical force varies as the velocity of motion imparted by it, we may perhaps conclude that this mechanical force is equal to 217 of the chemical force, and that the whole energy of the chemical action under the conditions of the experiment was equal to the mechanical power required to raise in the same period of time 160 times the weight of the Witherite altered to

the height of 1 metre. If these principles are correct, a pressure of more than 370 atmospheres would have entirely counterbalanced the force of chemical affinity, since to produce any chemical change it would then have had to overcome a greater force than it possessed. This is so great a pressure that I fear it will be difficult to prove the deduction by experiment; and until some such case can be found, capable of being verified, these calculations must be considered as little more than suggestions, which future investigations may confirm or disprove.

When calcite is sealed up in a mixed and rather strong solution of chloride of sodium and sulphate of copper, slow double decomposition gives rise to malachite, sulphate of lime, and carbonic acid; and though this case is extremely complicated, and it is very difficult to determine what would be the change in volume, yet, so far as I am able to make out, until the solution becomes saturated with sulphate of lime, there is a decrease in volume equal to about 8 per cent. of that of the calcite altered, so that, under pressure, mechanical force is the very reverse of being opposed to the chemical change. Three experiments, all indicating the same fact, and in which, on an average, the pressure was about 90 atmospheres for two weeks, show that, as a mean of the whole, the amount of chemical change was 17 per cent. more with the pressure than without; thus proving that pressure had, as it were, increased the force of chemical affinity. Calculating according to the principles described above, we may conclude that a pressure of 530 atmospheres would have caused the action to take place at double the rate, and that therefore the chemical action is equivalent to the expenditure of that amount of mechanical force, being thus generated by it. Arguing then in a manner similar to that already described, but modified to suit the different conditions, if there be a contraction equal to 8 per cent. of the bulk of the calcite, there must be a loss of mechanical force capable of raising 28 times the weight of the calcite altered to the height of 1 metre, in the time required for the chemical change; which amount of mechanical energy, as it were, becomes latent, and is transformed into chemical action, and would again exhibit itself as a mechanical force if, by any means, the chemical affinities could be inverted and everything restored to its original state.

In a like manner, other experiments indicate that in some cases

pressure causes a slower, and in others a quicker chemical action, whilst in others it has scarcely any influence whatever; and though, for reasons already explained, I say it with some hesitation, yet, bearing in mind what is already known respecting the action of pressure on hydrate of chlorine, hydrated hydrosulphuric acid, and other substances described by the various authors referred to in the notes, I think the facts I have described make it very probable that further research will show that pressure weakens or strengthens chemical affinity according as it acts against or in favour of the change in volume; as if chemical action were directly convertible into mechanical force, or mechanical force into chemical action, in definite equivalents, according to well-defined general laws, without its being necessary that they should be connected by means of heat or electricity. On the present occasion I shall not attempt to consider the various geological and mineralogical facts which appear to me to admit of the application of the principles I have described, for many of them are peculiarities in structure of which neither myself nor any one else has ever given a description, and would therefore demand a preliminary notice. However, I may say that it appears to me that a number of facts connected with metamorphic rocks and the phenomena of slaty cleavage, which, to me at all events, have hitherto been inexplicable, are readily explained if mechanical force be directly correlated to chemical action, and if in some cases the direction in which crystals are formed be more or less related to pressure, in some such way as there is a connexion between their structure and magnetic force, as shown by the experiments of Plücker, Faraday, Tyndall, and many other observers. We may also, I think, explain the origin of the impressions on the limestone pebbles in the "Nagelflue" in Switzerland, about which so much has been written in Germany and France, without a satisfactory reason having been discovered; and the same explanation accounts for the mutual penetration of the fragments of which some limestones are formed, and for the banded structure of some which possess slaty cleavage. The curious teeth-like projections with which one bed of limestone sometimes enters into another, also to a certain extent indicate a chemical action depending on mechanical force; and probably the same may be said of some of the peculiarities of slickensides and mineral veins. It is also possible that a pressure

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of several hundred atmospheres may facilitate some of the chemical changes involved in the transformation of water and carbonic acid into the organic compounds met with in animals and plants of low organization found at great depths in the ocean, and thus to a certain extent compensate for diminished light. I, however, most willingly admit that very much remains to be learnt before we can say to what extent the principles I have described are applicable; and yet, at the same time, cannot but think that henceforth they must be taken into account in many departments of chemical and physical geology, and will readily explain a number of facts which otherwise would be very obscure.

## May 7, 1863.

Major-General SABINE, President, in the Chair.

In accordance with the Statutes, the names of the Candidates recommended for election into the Society were read from the Chair, as follows:—

Edward William Cooke, Esq.,
A.R.A.
William Crookes, Esq.
James Fergusson, Esq.
Frederick Field, Esq.
Rev. Robert Harley.
John Russell Hind, Esq.
Charles Watkins Merrifield, Esq.
Professor Daniel Oliver.
Frederick William Pavy, M.D.

William Pengelly, Esq.
Henry Enfield Roscoe, B.A.
Rev. George Salmon, D.D.
Samuel James Augustus Salter, M.B.
Rev. Arthur Penrhyn Stanley, D.D.
Colonel Frederick M. Eardley Wilmot, R.A.

The following communications were read:-

I. "On the Physiological Properties of Nitrobenzole and Aniline." By Henry Letheby, M.B., F.L.S., &c., Professor of Chemistry, and late Professor of Toxicology in the Medical College of the London Hospital. Communicated by Dr. Sharpey, Sec. R.S. Received April 23, 1863.

It is on record that Thrasyas, the father of Botany, was so skilled in the preparation of drugs, that he knew how to compound a poison